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(54) Title of the Invention **Electron Emission Element and Method for Manufacturing Same**

[Claims]

[Claim 1] An electron emission element, comprising carbon nanotube electron sources and extraction electrodes and having a function of extracting and emitting electrons from said electron source by means of said extraction electrodes, wherein said electron emission element is characterized by a structure in which an anodic oxide film having pores is provided over an insulating substrate via a metal thin film, a metal catalyst is embedded in said pores, carbon nanotubes are grown using said metal catalyst as a starting point, and electron extraction electrodes are provided at the openings to said pores.

[Claim 2] A method for manufacturing an electron emission element, comprising the steps of:

forming an anodic oxide film having pores over an insulating substrate via a metal film;

depositing a metal catalyst in the pores of the anodic oxide film; and

growing carbon nanotubes in the pores of the anodic oxide film by the catalytic action of said metal catalyst.

[Claim 3] A method for manufacturing an electron emission element as defined in Claim 2, characterized by the use of an electrolytic pigmentation technique in the deposition of the metal catalyst in the pores of the anodic oxide film.

[Detailed Description of the Invention]

[0001]

Technological Field to Which the Invention Belongs

The present invention relates to an electron emission element that is used in displays, cathode ray tubes, emitters, lamps, electron guns, and so forth and exhibits superior current strength stability, and to a method for manufacturing this electron emission element.

[0002]

Prior Art

In recent years we have seen an increasing demand for thinner display devices and greater brightness, higher contrast, and wider vie wing angle of the images thereof. This has prompted a great deal of study into a switchover from conventional thermoelectronic emission electron sources to cold cathode electron sources for the electron sources used in display devices as well. For instance, as disclosed in Japanese Laid-Open Patent Applications H7-220619 and H7-94082 and elsewhere, a variety of cold cathode electron sources have been developed with a structure in which pores are provided to a metal oxide film and microscopic metal electrodes are disposed in these pores.

[0003]

Problems Which the Invention is Intended to Solve

For displays to have thinner films and better image quality, it is essential that the current strength per pixel be stable over time. However, there is considerable time fluctuation in the current values for the individual electron sources in conventional electron sources, and this problem needed to be overcome. Accordingly, the most important technical objectives are to suppress variance in the characteristics of the individual electron sources by increasing the number of electron sources per unit of surface area, and to raise the electron emission efficiency by reducing the radius of curvature of the tips of these electron sources, for instance. It is an object o f the present invention to solve the above problems and provide an electron emission element whose current strength is stable over time.

[0004]

Means Used to Solve the Above-Mentioned Problems

The present invention provides an electron emission element comprising carbon nanotube electron sources and extraction electrodes and having a function of extracting and emitting electrons from said electron source by means of the extraction electrodes, wherein this electron emission element is characterized by a structure in which an anodic oxide film having pores is provided over an insulating substrate via a metal thin film, a metal catalyst is embedded in the pores, carbon nanotubes are grown using the metal catalyst as a starting point, and electron extraction electrodes are provided at the openings to the pores. Current strength stability is superior because carbon nanotubes have such a small radius of curvature at their tips and also have high chemical stability. With the electron emission element of the present invention, the numerical density of the electron sources is raised, the outstanding characteristics offered by carbon nanotubes are fully exploited, and an improvement in current strength stability is achieved.

[0005] The invention defined in Claim 2 is the electron emission element according to Claim 1,[1] which is used in a display device. An electron emission element featuring carbon nanotubes has superior current strength stability, which affords a display with thinner films and better image quality when the element is used in a display device.

[0006] The invention defined in Claim 3 is the electron emission element according to Claim 1 or 2, characterized by having electron sources in the pores of an anodic oxide film. Current strength stability is superior because of the high numerical density of the electron sources.

[0007] The invention defined in Claim 4 is the electron emission element according to Claim 3, having a structure in which the anodic oxide film is formed on an insulating substrate via a metal thin film, carbon nanotubes are formed in said pores, and electron extraction electrodes are provided at the openings to said pores. The invention defined in Claim 5 is the electron emission element according to Claim 4, having a structure in which the pores of a plurality of anodic oxide films are regularly arranged. Electron emission elements having these structures have a higher numerical density of electron

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[1] Translator's note: There appear to be errors here and in sections 0006 and 0007, as the inventions described do not correspond to the Claims given, and there is no Claim 4 or 5. These errors are probably the result of amendments made to the original Claims.

sources and fully exploit the outstanding characteristics of carbon nanotubes, which affords an improvement in current strength stability.

[0008] The present invention also provides a method for manufacturing an electron emission element, comprising the steps of forming an anodic oxide film having pores over an insulating substrate via a metal film, depositing a metal catalyst in the pores of the anodic oxide film, and growing carbon nanotubes in the pores of the anodic oxide film by the catalytic action of said metal catalyst. With this method, the carbon nanotubes are arranged in a regular pattern, and the direction of the tips thereof is consistent.

[0009] It is preferable in the present invention to form the carbon nanotubes at a temperature of at least 1000°C and no higher than 1200°C. This method allows the carbon nanotubes to be formed in a size suited to disposition in the pores of an anodic oxide film.

[0010]

Embodiments of the Invention

The electron emission element of the present invention can be used in display devices, cathode ray tubes, emitters, lamps, electron guns, and so forth, but will be described below using a display device as a typical example. The structure of the electron sources is essentially the same regardless of the application.

[0011] Figure 1 is a cross section illustrating an example of the electron emission element of the present invention. In cross section, the structure has an alumina layer over a glass substrate, with an aluminum layer interposed, and pores that go all the way to the aluminum layer are provided in the alumina layer. A carbon nanotube grown using a metal catalyst as a starting point is present in each of the pores. Electrical power is supplied to these carbon nanotubes through the aluminum substrate, and these carbon nanotubes function as electron sources.

[0012] Nickel, cobalt, iron, and so forth can be used as the metal catalyst in the present invention.

[0013] The term "carbon nanotube" as used in the present invention refers to a graphite layer that is cylindrically wound in a form similar to telescoping tubes, having a thickness

of no more than a few dozen nanometers. The tubular shape can be seen in TEM observation. The radius of curvature of the tip portion is about 10 nm. In general, the tip of a cold cathode electron source must have a small radius of curvature so that strong electrolysis will be concentrated at the tip and the electron emission efficiency will be higher. Accordingly, a step in which the tip was tapered to a point was essential in prior art, and this required sophisticated technology and expert knowledge. In contrast, carbon nanotubes already have tips with a small radius of curvature, as mentioned above, so there is no particular need for the above-mentioned step, allowing an electron source with high electron emission efficiency and excellent current strength stability to be produced by a simple procedure. Carbon nanotubes also have excellent resistance to oxidation and ion impact, which keeps damage to the electron sources caused by ionization of residual gas to a minimum, and this also contributes to better current strength stability. Furthermore, because of their extremely small size, carbon nanotubes are favorable for producing a structure with less space between the electron sources. As will be discussed below, the numerical density of electron sources can be raised by a simple means such as forming carbon nanotubes in the pores of an anodic oxide film. This reduces variance in the characteristics of the individual electron sources and improves the stability of current strength per pixel.

[0014] While carbon nanotubes do offer these advantages, the following problems have been encountered in forming them. When carbon nanotubes were formed by a conventional method, the tips thereof tended to be oriented in different directions, and while bundling did allow the tips to be aligned in more or less the same direction, it was difficult to achieve a regular layout at a suitable spacing, and consequently it was difficult to produce a structure in which sufficient voltage could be applied to the individual carbon nanotubes.

[0015] In contrast, with the present invention, regularly arranged pores are formed by anodizing a metal such as aluminum, a metal catalyst is embedded in these pores, and this metal is used as a starting point in the growth of carbon nanot ubes, and this method solves the above-mentioned problems.

[0016] The electron emission element of the present invention is manufactured by the following method, for example. First, aluminum is anodized. This forms a regular

honeycomb structure of alumina of approximately 40 nm, with pores about 15 nm in diameter provided in the centers of the hexagonal cells (Figure 2). The size and spacing of the pores can also be varied by means of the type of electrolytic solution, the applied voltage, the temperature, and other such treatment conditions. This alumina layer is subjected to anisotropic etching until the bottoms of the pores reach the electroconductive aluminum substrate. Next, a metal catalyst is deposited using the electrolytic pigmentation technique used for aluminum window sashes. A solution of a sulfate, borate, or the like can be used as the metal salt solution in performing this electrolytic pigmentation. A supporting electrolyte, complexing agent, or other such substance that does not participate directly in the electrolysis may be added to the solution. The action of the catalyst thus embedded is to carbonize a hydrocarbon gas and grow carbon nanotubes having a specific direction and spacing on the aluminum substrate. Spaces are then created for separating the elements corresponding to the various pixels, a grid is made by slant vapor deposition, and metallization is provided for each pixel, thereby producing an electron emission element having ultrafine electron sources.

[0017]

Examples

Example 1

The electron emission element of the present invention was produced as follows. First, an aluminum film was formed over a flat glass substrate. This may be formed by either vapor deposition or application. The surface was then washed. This washing involved degreasing, rinsing with water, alkali etching, neutralization with an acid, and rinsing with water, in that order. The reason for neutralizing with an acid is that the alkali solution tends to remain behind after water rinsing, resulting in smut (a black powder).

[0018] The aluminum film was then anodized (alumite sulfate). The substrate washed as above was immersed in sulfuric acid with a concentration of 10%, and this product was used as an anode. An aluminum material was also used for the counter electrode, and

voltage was applied at DC 15 V. A film with a thickness of approximately 9 μm was obtained by leaving the power on for 20 minutes at a current density of 150 A/m^2.

[0019] After the treatment, anisotropic etching was performed by RIE (reactive ion etching) until the bottoms of the pores formed during the anodization treatment reached the aluminum substrate.

[0020] Next, electrolytic pigmentation was performed to deposit a metal catalyst inside the above-mentioned pores. A nickel sulfate solution (pH = 5) was used as the electrolytic solution. The substrate anodized as above was immersed in the electrolytic solution, power was applied for 1 minute at a voltage of 10 V and alternating current of 50 Hz using a carbon counter electrode, and nickel metal was deposited in the pores of the anodic oxide film. The amount of deposition can be controlled by varying the power-on time, voltage, solution concentration, and other factors.

[0021] After the nickel metal catalyst has been embedded in the pores as above, carbon nanotubes are grown by CVD using the apparatus shown in Figure 3. An alumina substrate is placed in the center of the tubular furnace in Figure 3, the degree of vacuum inside the furnace is held at 100 Torr while methane gas and hydrogen are supplied at 0.05 L/min and 0.02 L/min, respectively, and a heat treatment is conducted for 5 minutes at 1150°C. The reason for using hydrogen is to suppress the generation of amorphous carbon, which is a phase other than that of the carbon nanotubes. An inert gas can also be introduced in order to control the reaction time. Carbon nanotubes are formed at approximately 1000°C and above, but those having a diameter of about 10 nm, which is suited to the diameter of the pores in the alumina, are primarily formed at 1150°C. Heating to a temperature over 1200°C is undesirable because the diameter [of the tubes] will be on the order of microns.

[0022] A grid (extraction electrode) was then attached and element separation was performed in order to separate the various pixels, since [the product] will be used as a cold cathode electron source for display purposes. Element separation was performed by masking off and anisotropically etching the aluminum layer down to the glass (the supporting substrate), and the element dimensions for an electron source corresponding to one pixel were set at 1 × 1 μm. Within this surface area, there are approximately 2500 carbon nanotubes.

[0023] The electron emission element of the present invention was produced as above. This electron emission element was evaluated, which revealed that the stability of current strength over time was improved by approximately 50-fold compared to when conventional silicon or molybdenum was used and subjected to micro-working by lithography.

[0024] Example 2

In Example 1, the carbon nanotubes were contained within the pores as shown in Figure 1, but the carbon nanotubes may instead be grown longer so that their tips stick out of the pores.

[0025] Using the method for manufacturing an electron emission element illustrated in Example 1, the growth time was extended to 15 minutes in the CVD production of the carbon nanotubes, whereupon the tips stuck out of the pores. When the growth time was extended beyond 15 minutes, the nanotubes became curved. Care must therefore be taken in setting the proper growth time.

[0026] The grid that serves as the extraction electrode can be easily provided by using the type of metal mesh used in the masking of cathode ray tubes. Also, an insulating spacer was provided between the carbon nanotubes and the grid. Otherwise, the electron emission element was produced in the same manner as in Example 1.

[0027]

Effect of the Invention

With a conventional cold cathode electron source in which silicon, molybdenum, or the like was used, the spacing between the electron sources could not be any closer than about 1 μm due to limitations in micro-working. In contrast, with the present invention, the spacing between the electron sources is only about 40 nm, which is accomplished by forming carbon nanotubes serving as electron sources in pores made in an anodic oxide film. As a result, the numerical density of the electron sources is several thousand times greater than in the past, and the stability of current strength over time is approximately 50 times greater.

[0028] Carbon nanotubes also have excellent resistance to oxidation and ion impact, which keeps damage to the electron sources caused by ionization of residual gas to a minimum, so another advantage is that restrictions on the degree of vacuum of the electron emission element can be eased.

[0029] Furthermore, since no precise lithography is required with the present invention, the process is simplified.

Brief Description of the Drawings

Figure 1 is a cross section of the electron source array in the present invention;

Figure 2 is a diagram of the three-dimensional structure of the anodic oxide film; and

Figure 3 is a diagram of the apparatus used to grow carbon nanotubes by CVD.

Key:

1 grid

2 carbon nanotube

3 aluminum

4 fluorescent screen

5 metal catalyst

6 space element separation

7 pore

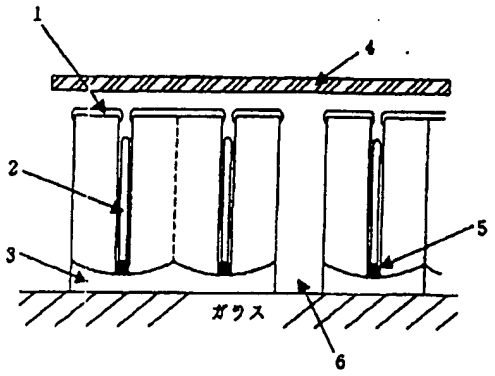
8 hexagonal cell

9 alumina

10 tubular electric furnace

11 alumina substrate containing metal catalyst

Figure 1



glass

Figure 2

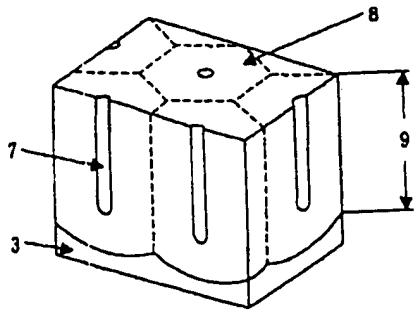
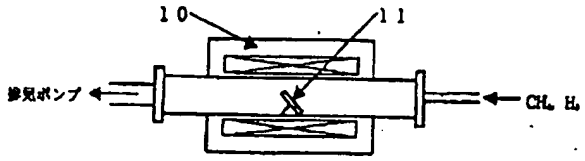


Figure 3



exhaust pump